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POLYMERIC HYDROSOLS COMPRISING AN UNSATURATED PROTEIN DERIVATIVE AND A COMBINATION OF UNSATURATED MONOMERS

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Our invention relates to polymeric hydrosols in which one of the components thereof is an unsaturated acid derivative of a protein. Our invention also relates to the compositions of those hydrosols with proteins particularly gelatin.

Gelatin when dry is characterized by a certain degree of brittleness. Hence various attempts have been made to improve the flexibility of gelatin by adding to coating compositions thereof flexibility improving materials. Many of these attempts have been unsatisfactory due to the fact that the materials added to the gelatin solutions have either been incompatible with the gelatin at some point in its use or themselves have exhibited brittleness. The use of gelatin particularly in sensitized photographic goods is wide spread at the present time and the improving of the flexibility of the gelatin has been desirable in many of those uses.

One object of our invention is to provide polymeric hydrosols which are compatible both with gelatin solutions and gelatin coatings under various conditions. Another object of our invention is to provide polymeric hydrosols in which unsaturated acid derivatives of protein are employed as one of the components in their preparation. A further object of our invention is to provide gelatin compositions with improved flexibility but with substantially the same refractive index as gelatin itself. A still further object of our invention is to improve gelatin by mixing therewith an aqueous dispersion of a polymer prepared by polymerizing an unsaturated derivative of a protein with an alkyl acrylate, the alkyl of which is at least two carbon atoms and a strengthening component. Other objects of our invention will appear herein.

We have found that polymeric hydrosols having the above and other properties are prepared by the emulsion polymerization of an unsaturated acid derivative of a protein with one or more alkyl esters of acrylic (the alkyl being of at least 2 carbon atoms) or methacrylic acid (the alkyl being of at least 4 carbon atoms) or butadiene, isoprene or chloroprene and one or more monomers which have strenthening properties. We have found that hydrosols as thus prepared can be mixed with gelatin in aqueous solution in all proportions, that no coagulation will occur in the preparation of coatings from gelatin solutions of this nature and that the coatings prepared from such compositions will have excellent flexibility and optical clarity, without decreasing the tensile strength of the gelatin. We have found that those polymeric hydrosols are compatible not only with the conventional photographic gelatins but also with hydrolyzed gelatins such as glue to produce compositions which will give clear flexible coatings upon coating out and drying.

These hydrosols or latices are prepared by the emulsion polymerization of a mixture of the reaction product of an unsaturated acid and protein, certain alkyl esters of acrylic or methacrylic acid (or butadiene, isoprene or chloroprene) and a strengthening component. The

protein compounds which have been found to be particularly useful in this connection are maleyl proteins, acrylyl proteins and methacrylyl proteins such as described in U. S. Patent No. 2,548,520 of Damschroder and Gates. The protein compounds which have been found to be most useful in our invention are those of gelatin either refined, e. g. photographic gelatin, or unrefined e. g. glue. The alkyl acrylate which is employed as a flexibilizer component of the polymer is one in which the alkyl (unsubstituted or substituted) is of at least 2 carbon atoms. Some of the acrylic acid esters which may be employed as the flexibilizing component in preparing hydrosols in accordance with our invention are ethyl acrylate, n-propyl acrylate, isopropyl acrylate isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-ethyl hexyl acrylate, β-cyanoethyl acrylate, hydroxy ethyl acrylate, chloroethyl acrylate, n-butyl acrylate, and hydroxy propyl acrylate. Also methacrylates of alkyls of 4–10 carbon atoms such as of n-butyl, n-hexyl, 2-ethyl hexyl or n-octyl, or butadiene, isoprene or chloroprene are useful as a flexibilizing component in preparing polymeric hydrosols in accordance with our invention. Either a single compound or a mixture of compounds as listed may be employed as the flexibilizing component.

The strengthening component may be any one or a mixture of a number of unsaturated monomers such as styrene, acrylonitrile, methyl acrylate, methyl methacrylate, ethyl methacrylate, o-methyl styrene, m-methyl styrene, p-methyl styrene, 2,4-dimethyl styrene, 2,5-dimethyl styrene, 3,4-dimethyl styrene, 3,5-dimethyl styrene, 2,4,5-trimethyl styrene, 2,4,6-trimethyl styrene, 2,4,5-triethyl styrene, o-ethyl styrene, m-ethyl styrene, p-ethyl styrene, 3,5-diethyl styrene, p-n-butyl styrene, m-sec-butyl styrene, m-tert-butyl styrene, p-hexyl styrene, p-n-heptyl styrene, p-2-ethylhexyl styrene, o-fluoro styrene, m-fluoro styrene, p-fluororstyrene, o-chloro styrene, m-chloro styrene, p-chloro styrene, 2,3-dichloro styrene, 2,4-dichloro styrene, 2,5-dichloro styrene, 2,6-dichloro styrene, 3,4-dichloro styrene, 3,5-dichloro styrene, 2,3,4,5,6-pentachloro styrene, m-trifluoromethyl styrene, o-cyano styrene, m-cyano styrene, m-nitro styrene, p-nitro styrene, p-dimethylamino styrene, α-chloroacrylonitrile, bromoacrylonitrile, α - trifluoromethyl acrylonitrile, α-trifluoromethyl carboxy acrylonitrile, vinyl acetate, vinylidene chloride and isopropenyl acetate.

If desired there may also be employed in preparing hydrosols in accordance with our invention 0–20%, based on the total monomer employed, of acrylic acid or acrylamide.

In preparing the polymeric hydrosols the protein derivative should be within the range of 14–60% based on the total monomer including the protein derivative employed in the preparation. The flexibilizer component, one or more of the alkyl acrylates mentioned, should be in the proportion of 1½–5 parts per part of the strengthening component. Instead of the unsaturated acid derivative of gelatin or glue there may be employed as the protein derivative the compound of some other protein acylated with an unsaturated acid, particularly one of casein or soy protein.

The preparation of the hydrosol is carried out in an aqueous system which preferably will contain a micell-forming surface active agent to facilitate the dispersion of the monomers therein. A catalyst, such as a per compound or a similar polymerization promoting material, is desirable to promote the reaction. The polymerization of the mixture of monomers is preferably carried out at an elevated temperature such as at 80° C. although a higher temperature may be employed. The use of excessive temperatures however is less desirable